A novel 2D bilayer architecture generated *via* π-π interactions and host–guest molecular recognition: assembly and structure of $\{[Cd(Htma)(bpy)(H_2O)]\cdot(H_2tp)_{0.5}\cdot 2H_2O\}_n$ polymer (tma = trimesate, bpy = 4,4′-bipyridine, tp = terephthalate)

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The interdigitation of the lateral tma ligands from two adjacent 4^4 nets *via* aromatic π-π interactions and host–guest molecular recognition gives rise to a novel 2D bilayer supramolecular architecture formed by the $\{[Cd(Htma)(bpy)(H_2O)]\cdot(H_2tp)_{0.5}\cdot 2H_2O\}_n$ polymer. An interested parallel/parallel interpenetration of the 4^4 net appears in this bilayer supramolecular architecture through other 2D H-bonded 4^4 nets formed by tma molecules that H-bond with water molecules. This compound, obtained from a hydrothermal reaction, crystallizes in the triclinic *P*-1 space group and exhibits a broad intense fluorescent emission upon photoexcitation at 311 nm.

Supramolecular chemistry based on metal-ion-directed assembly of organic molecular building blocks is receiving increasing attention owing to the potential discovery of novel functional materials, which are expected to find use in the areas of catalysis, nonlinear optics, sensors, magnetism and molecular recognition.[1] The discovery of new supramolecular frameworks using the principles of crystal engineering provides an important opportunity to explore assembly and structural diversity in the solid state.[2] In the construction of new supramolecular frameworks, coordination polymeric solids based on polycarboxylates are of special interest.[3] Many coordination polymers with interesting structures have been synthesized and characterized, such as the 1D zigzag chain,[4] 2D square network[5] and 3D open framework,[6] in which a novel structural motif called a molecular bilayer appears but such examples are still very limited.[7] Usually, the bilayer architecture has been fabricated by the assembly of T-shaped building blocks,[7,8] while rarely observed when other types of building blocks are used. In a previous report,[9] we demonstrated the one example of a bilayer architecture constructed by rectangular building blocks. Herein, we present another interesting example of the bilayer architecture constructed by a non-T-shaped building block in the cadmium(II)-tma-bpy hybrid ligand coordination polymer, $\{[Cd(Htma)(bpy)(H_2O)]\cdot(H_2tp)_{0.5}\cdot 2H_2O\}_n$ (**1**; tma = trimesate, bpy = 4,4′-bipyridine, tp = terephthalate), based on the π-π interactions of two rectangular networks and host–guest molecular recognition.

Experimental

All the chemicals were commercially purchased and used as received. Infrared spectra were recorded on a Magna 750 spectrometer using KBr pellets; elemental analyses were carried out by the Elemental Analysis Lab of the Fujian institute; fluorescent data were collected on an Edinburgh FL-FS920 TCSPC system by the Spectroscopy Lab of Fuzhou University. PXRD (powder X-ray diffraction) patterns were recorded on a Bruker AXS D8 advanced diffractometer at 40 kV, 40 mA with Cu Kα ($\lambda = 1.5406$ Å) radiation with a scan speed of $2°\cdot min^{-1}$ and a step size of 0.02° in 2θ by the X-Ray Diffraction Lab of Huaqiao University. TGA (thermal gravimetric analysis) were performed under nitrogen with a heating rate of 10 °C min^{-1} using a TA5200/MDSC2910 system by the Thermal Analysis Lab of Huaqiao University.

Synthesis of title compound

The title compound was synthesized hydrothermally in polytetrafluoroethylene lined stainless steel autoclaves under autogenous pressure. The static reaction of $Cd(O_2CCH_3)_2\cdot 2H_2O$, H_3tma, H_2tp, $bpy\cdot 2H_2O$ and H_2O in a molar ratio of 3:1:2:2:556 was allowed to proceed at 200 °C for 4 days, then the reactant mixture was cooled at a rate of *ca.* $3.5\,°C\cdot h^{-1}$ to give a 14% yield (based on Cd) of **1** as colorless crystals, which were collected by mechanical isolation and washed with water and absolute alcohol. The yield of **1** can be raised up to 68% or 70% by the same reaction using stoichiometric ratios of 2:2:2:1:556 or 3:3:3:1.5:556 instead of the above 3:1:2:2:556. Anal. calcd. (found): C, 45.00 (45.21); O, 28.67 (27.90); H, 3.45 (3.33); N, 4.56 (4.30). IR (KBr pellet, cm^{-1}): 3345 (m, br), 3082 (vw), 3055 (w), 1714 (vw, sh), 1695 (m), 1620 (m), 1603 (vs), 1578 (vw), 1558 (w), 1541 (vw), 1491 (m), 1435 (m), 1416 (m), 1369 (vs), 1265 (m), 1221 (s), 1190 (w), 1101 (w), 1076 (m), 1043 (w), 1007 (m), 935 (w), 806 (s), 758 (s), 729 (m), 692 (m), 631 (s), 517 (w), 490 (w).

Table 1 Selected crystal parameters, data collection and structure refinement for **1**

Formula	$C_{23}H_{21}CdN_2O_{11}$
Formula weight	613.82
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.1284(4)
b/Å	11.1119(4)
c/Å	11.7224(4)
α/deg	109.5190(10)
β/deg	95.9500(10)
γ/deg	105.4250(10)
U/Å^3	1171.47(7)
Z	2
μ/mm^{-1}	0.999
T/K	293(2)
λ(Mo-$K\alpha$)/Å	0.71073
Collected reflections	6120
Independent reflections	4097
Observed reflections	3353 [$I > 2\sigma I$]
R_{int}	0.0277
R^a	0.0563 (for obs.)
$R_w{}^b$	0.1414 (for obs.)

[a] $R = \sum(\|F_o| - |F_c\|)/\sum|F_o|$. [b] $R_w = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o{}^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3]$.

Crystallographic studies

Intensity data was collected on a Siemens Smart CCD diffractometer. The structure was solved by direct methods using SHELXS-97[10] and was refined by full-matrix least-squares methods using SHELXL-97.[11] Anisotropic displacement parameters were refined for all non-hydrogen atoms except for the disordered guest water molecules. No attempt was made to locate the hydrogen atoms of water; the other hydrogen atoms were added in the riding model and were not refined. The crystallographic data are summarized in Table 1; selected interatomic distances and angles are presented in Table 2. CCDC reference number 191055. See http://www.rsc.org/suppdata/nj/b3/b300223c/ for crystallographic files in CIF or other electronic format.

Results and discussion

Compound **1** was formulated as $\{[Cd(Htma)(bpy)(H_2O)]\cdot(H_2tp)_{0.5}\cdot 2H_2O\}_n$ on the basis of the elemental analysis. This compound is very stable in air at ambient temperature and is almost insoluble in common solvents such as water, alcohol, acetonitrile and acetone. The synthetic reproducibility of compound **1** is very nice. The yield of **1** can be raised up to 68–70% when the synthesis is repeated with different ratios of the reactants. This implies that the synthesis of **1** is not so rigorous in its stoichiometry demands, like some other products resulting from hydrothermal reactions. The IR spectrum of **1** shows the characteristic bands of the tma ligand at 1603 cm^{-1} for the asymmetric vibration and at 1369 cm^{-1} for the symmetric vibration, as well as the bands of the bpy ligand at 1451, 1578, 1558, 1416, 1435 and 1491 cm^{-1} for the stretching vibration of the C–N and C–C bonds. The broad band at 3345 cm^{-1} and the sharp band at 1620 cm^{-1} indicate the presence of coordinated water molecules,[4a] while the bands at 1714 and 1695 cm^{-1} suggest the presence of a protonated carboxylate group. These are in good agreement with the structure of **1**.

Table 2 Selected bond lengths (Å) and bond angles (deg) for **1**[a]

Cd(1)–N(2a)	2.321(6)	Cd(1)–O(12)	2.382(5)
Cd(1)–N(1)	2.338(5)	Cd(1)–O(11)	2.457(5)
Cd(1)–O(15b)	2.355(5)	Cd(1)–O(16b)	2.526(5)
Cd(1)–O(10)	2.364(5)		
N(2a)–Cd(1)–N(1)	174.7(2)	N(1)–Cd(1)–O(11)	95.8(2)
N(2a)–Cd(1)–O(15b)	90.6(2)	O(15b)–Cd(1)–O(11)	132.68(17)
N(1)–Cd(1)–O(15b)	89.17(19)	O(10)–Cd(1)–O(11)	81.1(2)
N(2a)–Cd(1)–O(10)	89.5(2)	O(12)–Cd(1)–O(11)	53.13(17)
N(1)–Cd(1)–O(10)	87.76(19)	N(2a)–Cd(1)–O(16b)	92.6(2)
O(15b)–Cd(1)–O(10)	146.2(2)	N(1)–Cd(1)–O(16b)	83.06(18)
N(2a)–Cd(1)–O(12)	96.2(2)	O(15b)–Cd(1)–O(16b)	53.32(15)
N(1)–Cd(1)–O(12)	88.94(19)	O(10)–Cd(1)–O(16b)	92.93(18)
O(15b)–Cd(1)–O(12)	80.07(17)	O(12)–Cd(1)–O(16b)	132.63(16)
O(10)–Cd(1)–O(12)	133.5(2)	O(11)–Cd(1)–O(16b)	173.96(16)
N(2a)–Cd(1)–O(11)	88.2(2)		

[a] Symmetry transformations used to generate equivalent atoms: a = x, y, $z+1$; b = $x+1$, y, z.

The crystal structure of **1** consists of a 2D bilayer architecture based on the π-π interactions of two 4^4 nets whose fundamental building unit contains a 7-coordinated Cd(II) center, a tma ligand and a bpy ligand (Fig. 1). In the building unit of **1**, the Cd(II) center is in a distorted pentagonal bipyramidal environment, completed by two nitrogen atoms (N1, N2a) of two bpy ligands as the apices and five oxygen atoms in the equator, of which one is from a water molecule (O10) and the other four belong to two chelating bis-bidentate carboxylate groups (O11 and O12, O15b and O16b) of two tma ligands. On the other hand, each tma ligand and bpy ligand link two different Cd(II) centers through two chelating carboxylate groups and two nitrogen atoms, respectively. The Cd–O bond distances range from 2.355(5) to 2.526(5) Å, while the Cd–N bond distances are 2.321(6) and 2.338(5) Å (see Table 2). The remaining carboxylate group in the tma ligand is uncoordinated. In addition, a H_2tp guest molecule and two water molecules [(O01, O02, O03) and O04] are not linked to the building unit; one water molecule shows positional disorder of the O atom (O01, O02, O03) over three sites (Fig. 1). In the coordination sphere, due to the effect of the terminal water molecule (O10), the angle between two adjacent carboxylate groups (C17···Cd1···C19b) of two tma ligands chelated to the same Cd(II) center is 132.07° rather than 180°, thus these two adjacent tma ligands fall into rank in a 'hand in hand' fashion (Fig. 1). In this way, each fundamental building unit of the crystal structure is linked to another to generate a 2D rectangular grid layer, regarded as a typical 4^4 net, with a 10.13 × 11.72 Å window, in which the lateral tma ligand orients vertically up or down in a layer (Fig. 2).

Interestingly, the actual crystal structure of **1** is a framework stacking in such a manner that two adjacent 4^4 nets are further interdigitated into each other along the direction of the uncoordinated carboxylate group of the lateral tma ligands to fabricate a novel 2D bilayer supramolecular architecture [Fig. 3(a–c)] showing an effective aromatic π-π interaction[12] between the two lateral tma ligands of two adjacent 4^4 nets [face-to-face distance of 3.63 Å, Fig. 3(d), Fig. 4], resulting in inner cavities of *ca.* 10.13 × 7.30 Å, which are clathrated with guest H_2tp and water molecules [Fig. 3(a,c)]. The effective cavities in the actual crystal structure of **1**, after the removal of the two water clathrate molecules (O01, O02, O03, O04), has a volume of only *ca.* 44 Å^3, which is 3.7% of the unit cell volume, although the single 4^4 net contains a big window as described above. This is, to our knowledge, the first example of bilayer architecture assembled *via* aromatic π-π stacking interactions.

It is notable that the aromatic face-to-face distance of 3.60 Å between H_2tp guest molecule and lateral tma ligand of the host framework [Fig. 3(d), Fig. 4] reveals a strong π-π stacking interaction of these related aromatic rings from host–guest molecules. This suggests that the host–guest molecular recognition, especially the H_2tp guest molecule, plays an important role on the assembly of bilayer architecture of **1**. In additional, these aromatic π-π stacks show offset or slipped packing rather

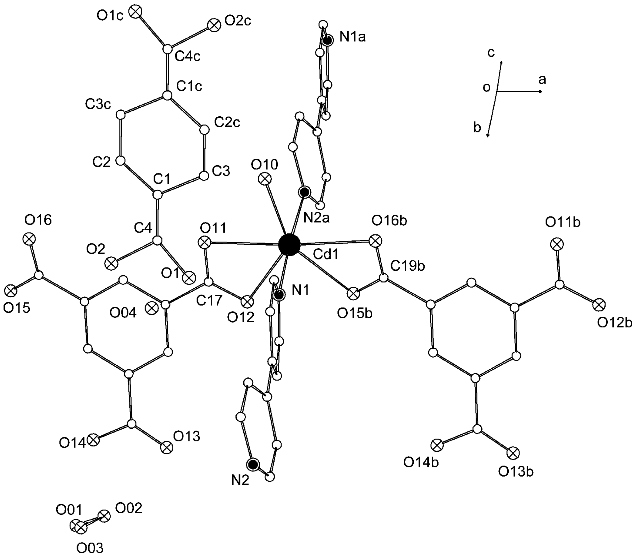

Fig. 1 A view of **1** depicting the coordination environment around the Cd(1) center, the hydrogen atoms are omitted for clarity. Symmetry code: a = $x, y, z+1$; b = $x+1, y, z$; c = $-x, -y, -z$.

than a perfect face-to-face array of the atoms; the centroid···centroid contacts between two overlapping tma aromatic rings and between tma and H_2tp aromatic rings are 4.40 and 3.75 Å, respectively (Fig. 4), which are available for increasing stability in the interaction of π-π framework stacking due to the contribution of π-σ attraction (*i.e.*, aromatic CH···π interaction).[12d]

Especially interesting, the guest H_2tp molecules of adjacent bilayers interact by strong H-bonds (O···O distances range from 1.9 to 2.8 Å) with guest water molecules (O04) forming inclined 1D chains interpenetrating the bilayers. Moreover, a remarkable parallel/parallel interpenetration of 4^4 nets can be observed in the architecture of **1**, which occurs when 2D H-bonded 4^4 nets generated by the tma molecules H-bond adjacent bilayers through water ligand molecules (O10; strong H-bond: O···O = 2.7 Å) and disordered guest water molecules (O01, O02, O03; weaker H-bonds: O···O distances range from 2.6 to 2.9 Å) (Fig. 5). To our knowledge, such an interpenetrated network has not been reported to date.

The TGA trace of **1** shows two obvious weight losses. The first weight loss started at *ca.* 58 °C and lasted up to 111.4 °C, centered at 93.6 °C, with a total weight loss of *ca.* 8.7%, corresponding to the loss of three H_2O molecules per formula unit. This suggests that these water molecules should be lattice water. The complete decomposition of **1** occurred as another weight loss in the 383.1–538.5 °C range, showing that the framework of **1** is rather stable. The PXRD patterns of

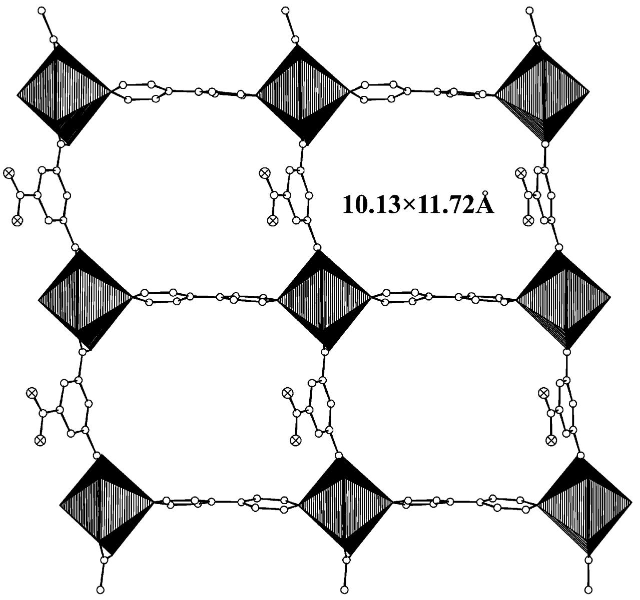

Fig. 2 A view of a single 4^4 net in **1** showing the 2D rectangular grid layer with a 10.13 × 11.72 Å window and the lateral tma ligand pointing vertically up from the layer, the hydrogen atoms are omitted for clarity.

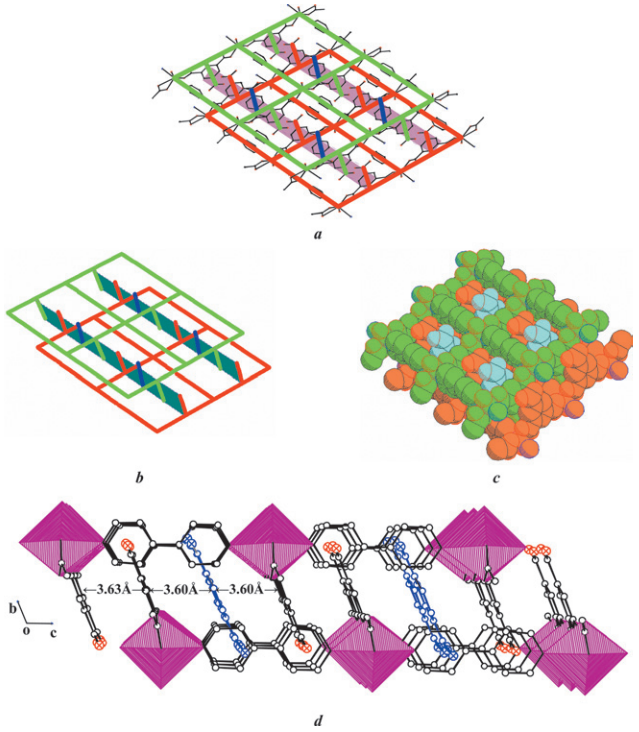

Fig. 3 (a) A view of the 2D bilayer supramolecular architecture in **1** assembled by the aromatic π-π interactions of two adjacent 4^4 nets and guest H_2tp molecules (in blue). (b) Schematic diagram showing a pillared bilayer motif based on **1**. (c) Space-filling view of the 2D bilayer supramolecular architecture in **1**. (d) Side view along the *a* axis showing the face-to-face π-π interactions between the aromatic rings of guest H_2tp molecules (in blue) and the lateral tma ligands of two adjacent 4^4 nets in **1**. Hydrogen atoms and aqua guests are omitted for clarity.

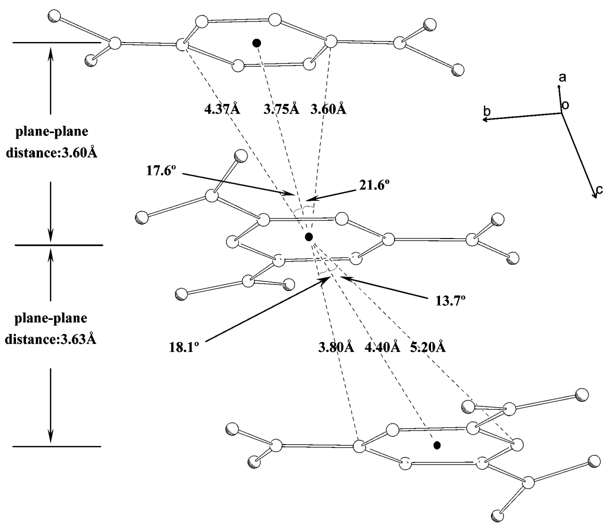

Fig. 4 Schematic diagram showing the offset of the baricentres of three aromatic rings in **1**.

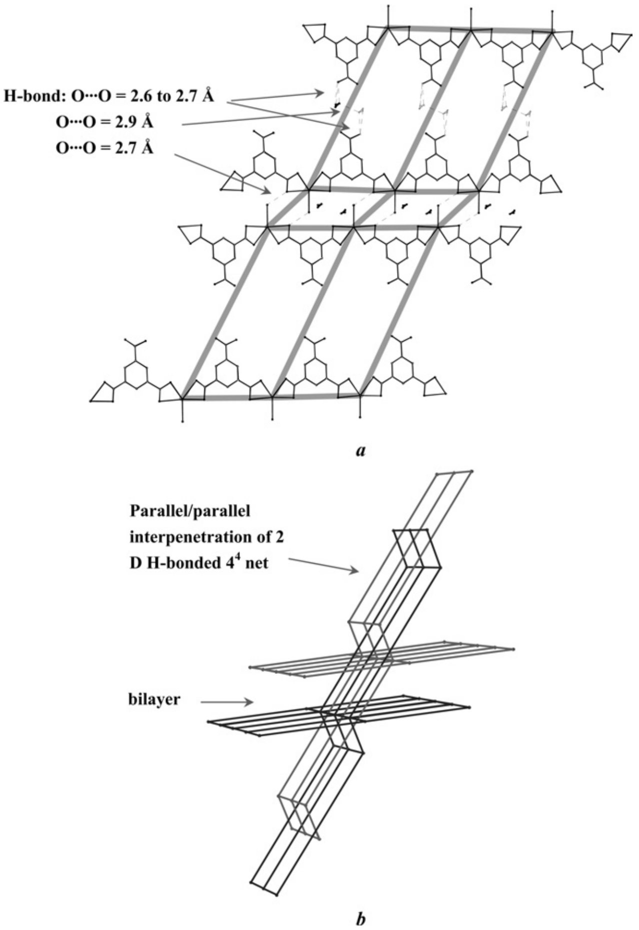

Fig. 5 (a) A 2D H-bonded 4^4 net fabricated by the tma molecules of adjacent bilayers H-bonding through water ligand molecules (O10) and disordered guest water molecules (O01, O02, O03) in **1**. (b) Schematic diagram showing a remarkable parallel/parallel interpenetration of 2D H-bonded 4^4 nets based upon **1**.

heated solid were obtained to study the stability of guest removal/readsorption. Compared to the original crystals, the dehydrated solid obtained by heating crystals of **1** to 200 °C shows an almost identical PXRD pattern as far as the line positions are concerned but the intensity is weakened. Interestingly, the intensity of the lines can be partially recuperated after this dehydrated solid is immersed in water. This suggests that the dehydration of **1** is reversibe. However, further heating of the solid to 383 °C results in changes in both the line positions and the intensities of the PXRD pattern and the PXRD pattern of the original crystals cannot be recovered by immersion in water. This indicates that collapse of the whole framework of **1** occurs, which is consistent with the TGA results above.

Upon excitation in the UV at 311 nm an intense fluorescent emission spectrum of **1** in the solid state at room temperature is observed in the visible region at 360, 416, 481 and 513 nm (λ_{ex} = 311 nm), assigned as ligand-to-metal charge-transfer (LMCT) bands. Surprisingly, the emission of **1** is not only intense but also broad, with wavelength ranging from the visible blue to green region of the spectrum, as compared with some other related polymers.[7b,9] The interesting luminescence property is probably connected to the structural phenomenon of aromatic π-π stacking interactions.[12d,13] This implies that **1** will be an excellent candidate for potential photoactive materials.

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